DIFFUSIVITY OF CARBON DIOXIDE IN ETHANOL-WATER MIXTURES

J. SIMONS² AND A. B. PONTER^{*1}

Chemical Engineering Institute, Swiss Federal Institute of Technology of Lausanne, Lausanne, Switzerland

Diffusion coefficients of carbon dioxide in aqueous ethanol solutions have been determined at 25°C and at atmospheric pressure, using a short wetted-wall column.

The diffusional behaviour is compared with both that predicted by equations containing a relationship between diffusivity and liquid viscosity and equations correlating diffusivities to the values for the pure components of a binary liquid.

The diffusional behaviour at low ethanol concentrations is compared with other physical changes occurring at these conditions such as the wetting properties, partial molal volumes, sound velocity etc., to provide some insight into the combined effect of relative molecular size and hydrogen bonding on the diffusional mechanism.

Introduction

When diffusion plays a decisive role in an industrial process plant, design is often based on limited experimental data or empirical equations predicting a relationship between diffusivity and liquid viscosity.

The kinetic theory of Arnold⁽³⁾ predicts that the diffusivity is inversely proportional to the square root of viscosity while the activated rate process⁽⁹⁾ and hydrodynamic⁽⁸⁾ approaches predict an inverse dependence on viscosity. A review of the relationship between diffusivity and solvent viscosity in dilute liquid solutions by Hayduk and Cheng⁽¹²⁾ shows that they are not inversely related but that the diffusivity depends on the solvent viscosity raised to some power which is variable, depending on the diffusing substance. Akgerman and Gainer^(1,2) have demonstrated the inadequacy of theories to predict diffusivities which do not take into account molecular interactions and geometrical considerations.

In this Department an investigation was carried out to ascertain why the distillation performance of film contacting devices deteriorates at low compositions which revealed that very significant wetting changes occurred in this region⁽²⁵⁾, attributed to a closer packing of molecules at the interface at a concentration corresponding to a minimum value of the partial molar volume. For design purposes therefore the point arises as to whether both the influential bulk property, namely diffusivity, as well as the sur-

face properties will change substantially at near-terminal compositions.

An experimental program which is now described was proposed to measure the diffusivities of carbon dioxide in ethanol/water mixtures to ascertain by a simple experimental technique whether the molecular packing would influence the diffusivity to an extent which would justify the more difficult determination of ethanol diffusion into aqueous solutions under distillation conditions.

Experimental

The diffusion coefficients were determined at 25.0°C and atmospheric pressure by measuring gas absorption rates using a short wetted-wall column of outer diameter 2.720 cm and adjustable length 0~6 cm. The decrease in gas volume during the absorption was measured by means of a soap-bubble meter. Liquid mixtures were made up gravimetrically and compositions checked from tabulated density data⁽³⁰⁾, the precision being 0.01 mole% ethanol. The purity of the ethanol employed was better than 99.8%, the water was double distilled in a quartz unit and the carbon dioxide had a minimum purity of 99.7%.

The liquid flow rates were controlled with a precision of more than 0.3% and the temperature within 0.05°C. The driving force for the liquid flow was obtained by an overpressure of nitrogen gas. The solubility of nitrogen in water-ethanol mixtures is extremely low⁽¹³⁾ and will not influence the diffusivity.

The carbon dioxide gas was saturated with the solvent to prevent transfer of liquid at the film surface before entering the absorption chamber.

Absorption rates were determined for a number of liquid compositions, using three different column

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¹ Address for correspondence: Institut de génie chimique, En Vernay, CH-1024 Ecublens, Switzerland.

² Laboratorium voor chemische technologie, Universiteit van Amsterdam, Nederland

Fig. 1 Diffusivity of carbon dioxide into aqueous ethanol mixtures at 25°C

Fig. 2 Plot of D and $D\mu$ versus mol fraction

Fig. 3 Comparison of predicted and experimental values of diffusivity

Table 1 Diffusivity of carbon dioxide/water at 25°C	
$D \times 10^5$ [cm ² /sec]	Source
1.85	Maharajh and Walley (19)
1.90	Davidson and Cullen (6)
1.92	Cullen and Davidson (5)
1.94	Experimental
1.95	Thomas and Adams (29)
1.98	Duda and Vrentas (7)
1.99	McManamey and Woollen (20)
2.02	Jeffreys and Bull (15)

lengths from 1 up to 6 cm, and four different liquid flow rates from about 1.5 to 5 ml/sec. These column lengths and flow rates were chosen so that the penetration depth was small compared with the film thickness and rippling and film mixing were avoided.

Theory

For small penetration depths the gas absorption rate into a laminar liquid film flowing down a vertical tube is given by

$$q_A = 2dC_{A0}h(\pi D_{AB}/t_c)^{1/2} \quad (1)$$

with the contact time being given by

$$t_c = 2/3 h \left(\frac{3\mu\pi^2 d^3}{\rho g Q^2} \right)^{1/3} \quad (2)$$

Equations (1) and (2) combine to give

$$D_{AB} = \frac{q_A^2}{C_{A0}^2 h} \left(\frac{\mu}{72\pi\rho g d^4 Q^2} \right)^{1/3} \quad (3)$$

As the measured decrease in gas volume y also comprises the condensed liquid vapours, the absorption rate of carbon dioxide will be

$$q_A = \frac{P \cdot y}{RT} \cdot \frac{P_A}{P} \quad (4)$$

assuming ideal gas behaviour.

Since

$$C_{A0} = P_A \cdot C'_{A0} \quad (5)$$

where C'_{A0} is the saturation concentration of carbon

dioxide at 1 atm partial pressure, substitution of Eqs. (4) and (5) into Eq. (3) gives

$$D_{AB} = \left(\frac{1}{RT C'_{A0}} \right)^2 \cdot \left(\frac{\mu}{72\pi\rho g d^4} \right)^{1/3} \cdot \left(\frac{y^2}{h} \right) \cdot \left(\frac{1}{Q} \right)^{2/3} \quad (6)$$

End effects were calculated and taken into account by measurement of the abscissa of the y^2 versus h graphs at $y^2=0$ and never accounted for more than 20% of the total column length.

Results and Discussion

Initially the diffusivity of carbon dioxide into water was determined at 25°C. The value of 1.94×10^{-5} cm²/sec obtained is in good agreement with reported data as indicated in Table 1.

The diffusivities obtained for the ethanol-water system are shown in Fig. 1. Calculated values were based on viscosity data taken from Lange¹⁶⁾ and carbon dioxide solubilities from Seidell *et al.*²⁷⁾ and Linke¹⁸⁾. The diffusivities expressed as a function of liquid composition, show an initial decrease of D with increasing ethanol concentration, with a minimum at about 13 mole% ethanol. The product $D\mu$ is also shown in Fig. 2, demonstrating a sharp initial increase with ethanol concentration, reaching a flat maximum at about 60 mole%. The maximum value of $D\mu$ is 200% higher than the minimum value, demonstrating the inadequacy of the Stokes-Einstein relation and other equations which predict a constant value of $D\mu$. Also $D\mu^{1/2}$ varies enormously (between 1.77×10^{-7} and 4.71×10^{-7}). It is not possible at the present time to relate the position of the minimum in D or the maximum in $D\mu$ to the solvent properties only, as shown by comparing three other reported diffusivities at 25°C in the same solvent: Perkins and Geankoplis²⁴⁾ observed a maximum in $D\mu$ at 15 mole% ethanol, the diffusing species being acetic acid. Nakanishi and Ozasa²¹⁾ observed a

pronounced maximum near 10 mole % for the diffusion of iodine. In both systems the diffusing component was very dilute. Pratt and Wakeham²⁶⁾ investigated the mutual diffusion of ethanol in ethanol/water (not being the intradiffusion) at 25°C and observed a minimum in D at 30 mole % and two maxima for $D\mu$ at 5 and 80 mole % ethanol (the concentration gradient not being reported). At near terminal compositions (small ethanol concentrations) all the four systems investigated show a sharp decrease in D with increasing ethanol concentration, which corresponds to an increase in the activation energy in terms of the rate process model. To provide further insight into the diffusional mechanism, this behaviour may be compared with changes in some structural and physical properties of the ethanol/water system at near terminal composition, as reported by Franks¹⁰⁾ and Franks and Ives¹¹⁾. They showed:

- a sharp decrease in the excess enthalpy of mixing, with a minimum value at 17 mole % ethanol.
- a sharp decrease in the partial molar volume with a minimum value at 8 mole % ethanol.
- a flat maximum in the excess sound absorption at 8 mole % ethanol.
- a maximum in the velocity of sound at about 15 mole % ethanol.
- a sharp increase in viscosity with a maximum value at about 27 mole % ethanol.

Ponter *et al.*²⁵⁾ studied the wetting properties of the ethanol water system on a high energy surface and reported a sharp increase in contact angle at about 2 mole % ethanol. From the abnormal physical properties of water, such as the high latent heat of evaporation, and from infrared spectroscopy it is well known that association of water molecules occurs by hydrogen bonding, determining predominantly the structure. Frank and Ives concluded that hydrogen bonds have also profound effect on the properties of ethanol, the molecular structure being strongly effected by steric limitations. The solubility of carbon dioxide in the solvent, which is (as the diffusivity) determined by the liquid structure and by interaction between all the components, shows remarkable qualitative agreement with the diffusivity, but a simple relationship could not be found.

Attempts have been made to correlate the diffusion coefficient for a dilute species in a binary liquid mixture to the diffusivities in the pure components. Bird, Stewart and Lightfoot⁴⁾ derived an equation from the Stefan-Maxwell relations:

$$D_{1m} = 1 / \left(\frac{x_2}{D_{12}} + \frac{x_3}{D_{13}} \right) \quad (7)$$

Four other equations have been derived from the absolute rate theory, but using different mixing rules

for viscosity and questionable simplifications: Holmes, Olander and Wilke¹⁴⁾:

$$D_{1m} \cdot \mu_m = x_2 D_{12} \mu_2 + x_3 D_{13} \mu_3 \quad (8)$$

Olander²³⁾:

$$D_{1m} \cdot \mu^{1/2} = x_2 D_{12} \mu_2^{1/2} + x_3 D_{13} \mu_3^{1/2} \quad (9)$$

Leffler and Cullinan¹⁷⁾:

$$\log(D_{1m} \cdot \mu_m) = x_2 \log(D_{12} \cdot \mu_2) + x_3 \log(D_{13} \cdot \mu_3) \quad (10)$$

Tang and Himmelblau²⁸⁾:

$$\log(D_{1m} \cdot \mu_m^{1/2}) = x_2 \log(D_{12} \cdot \mu_2^{1/2}) + x_3 \log(D_{13} \cdot \mu_3^{1/2}) \quad (11)$$

Figure 3 shows a comparison of all these equations with experimental data with Eq. (9) giving the best agreement. No conclusion however can be drawn, as Eqs. (7) to (11) have been shown to be valid for other systems investigated. Nakanishi, Ozasa and Ashitani²²⁾ investigated the diffusion of iodine in a variety of binary solvents containing ethanol and found that none of the above equations would correlate the data of all the systems examined.

Conclusions

Experimental data from this investigation show that any D - μ relationship fails when generally applied, especially for highly non-ideal systems such as CO₂-ethanol-water. Hence equations based on the hydrodynamic theory⁸⁾ or the kinetic theory of Arnold³⁾ will lead to large errors as expected since the processes of diffusive and viscous flow are fundamentally different.

The theory developed by Akgerman and Gainer^{1,2)} takes into account molecular interaction as well as solvent viscosity, and represents the most successful approach presented in the literature to date.

No equation can be recommended to correlate the diffusion coefficient in a binary liquid mixture to the values for the pure component, although Eq. (9) gives the best agreement for the system investigated. The reduction in diffusivity with increasing alcohol concentration at near-terminal compositions for the carbon dioxide-ethanol-water system suggests that similar behaviour will result during the distillation of ethanol-water mixtures. Therefore the reduction in efficiency observed in packed columns at low ethanol concentrations can now be attributed not only to the changes in wetting (which reduces the interfacial area between liquid and vapor available for mass transfer²⁶⁾) but also to the significant lowering in diffusivity.

Nomenclature

C_A	= molar concentration of A	[mol/ml]
C_{Ao}	= C_A for saturated liquid	[mol/ml]
C'_{Ao}	= C_{Ao} at $P_A = 1$ atm	[mol/ml]
D_{AB}	= effective diffusion coefficient	[cm ² /sec]
d	= diameter of column	[cm]
g	= gravitation constant	[cm/sec ²]

h	= height of column	[cm]
M	= molecular weight	
N_{Ax}	= molar flux in x -direction	[moles/cm ² ·sec]
P	= pressure	[atm]
Q	= liquid flow rate	[ml/sec]
q_A	= gas absorption rate	[mole/sec]
R	= gas constant	[ml·atm/mol·°K]
T	= absolute temperature	[°K]
V	= molar volume	[cm ³ /mol]
x_i	= mol fraction of component i	
y	= gas absorption rate	[ml/sec]
ρ	= liquid density	[g/ml]
μ	= liquid viscosity	[g/cm·sec]

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SELF-DIFFUSION IN LIQUID METALS

MAKOTO HARADA*, MASATAKA TANIGAKI,
YUICHI TOYOTA AND WATARU EGUCHI
Institute of Atomic Energy, Kyoto University, Uji, 611

The relaxation model previously proposed by the authors was applied to the self-diffusion process in liquid metals. A Lennard-Jones type pair potential function was used to evaluate the term related to the frequency of the oscillatory motion in liquids. The self-diffusivity of liquid metals can be calculated simply from the melting temperature, T_m , and the liquid density, ρ , with the use of the final formulae:

$$D = 0.135z(kT)^{1/2}m^{-1/6}\rho_0^{-1/3}(T/T_m)^{1/2}(1-\rho/\rho_0) = 0.555(kT)^{1/2}m^{-1/6}\rho_m^{-1/3}(T/T_m)^{1/2}(1-\rho/1.068\rho_m)$$

The agreement of calculated values with observed ones is satisfactory, especially for temperature dependency. The physical meaning of the model parameters, z and ρ_0 is also discussed.

Introduction

Transport properties of liquid metals are im-

portant in metallurgical and in nuclear industrial processes. Among them, self-diffusivity is the most fundamental one and gives insight into the nature of the liquid state. Though liquid metals are mono-

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